

# Evaporation of buffer gas-thermalized anions out of a multipole rf ion trap

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We identify plain evaporation of ions as the fundamental loss mechanism out of a multipole ion trap. Using thermalized negative  $\text{Cl}^-$  ions we find that the evaporative loss rate is proportional to a Boltzmann factor. This thermodynamic description sheds new light on the dynamics of particles in time-varying confining potentials. It specifically allows us to extract the effective depth of the ion trap as the activation energy for evaporation. As a function of the rf amplitude we find two distinct regimes related to the stability of motion of the trapped ions. For low amplitudes the entire trap allows for stable motion and the trap depth increases with the rf field. For larger rf amplitudes, however, rapid energy transfer from the field to the ion motion can occur at large trap radii, which leads to a reduction of the effective trapping volume. In this regime the trap depth decreases again with increasing rf amplitude. We give an analytical parameterization of the trap depth for various multipole traps that allows predictions of the most favorable trapping conditions.

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Evaporation of atoms and molecules out of a confined thermalized ensemble is a well understood process [1, 2] and represents the decisive cooling step towards Bose-Einstein condensation [3, 4]. In radiofrequency (rf) ion traps, early studies of the dynamics have shown that, in the absence of a buffer gas, thermalization is achieved by ion-ion collisions and evaporative losses [5, 6]. In applications of rf Paul traps [7] for quantum information processing [8, 9], precision spectroscopy [10, 11, 12], and the production of translationally ultracold molecular ions [13, 14], trapped ions are cooled using light forces. For the sympathetic cooling of ions in a buffer gas, higher order multipole rf traps at cryogenic temperature have proven to be more useful due to their large field free region [15, 16]. Multipole ion traps are hence widely used to prepare cold molecular ions in laboratory astrophysics [17], to reduce the Doppler shift in microwave ion clocks [18], to measure absolute photodetachment cross sections of molecular anions [19], the photofragmentation of biomolecules [20], for precision rovibrational spectroscopy [21, 22, 23] and for collision experiments [24].

If the ion temperature is fixed by collisions with a buffer gas, evaporative loss measurements provides access to the stability of ion motion in traps. In a quadrupole or Paul trap, stable ion motion is described analytically by the Matthieu equations, which puts well-defined constraints on the trapping fields. In addition to these global boundaries of stability, heating of trapped ions by the rf field might be assisted or damped by Coulomb interaction, and phase transitions between crystalline and chaotically moving clouds are observed [25]. In contrast, for ions moving in a high order multipole field the equations of motion have no analytical solution. There have been

attempts to numerically establish a stability diagram for two-dimensional hexapoles and octupoles [26]. For different starting conditions the obtained stability diagrams look very different and the regions of stability do not show well defined boundaries opposite to the case of the quadrupole trap.

In this letter we show that one can attribute in a thermodynamic sense an effective trap depth to an ion cloud in a multipole ion trap. For this purpose we measure the rate of evaporation of trapped ions as a function of their translational temperature controlled by a bath of helium buffer gas. We use  $\text{Cl}^-$  anions with a high electron affinity, because one can safely ignore losses due to parasitic chemical reactions with the background gas. The measured evaporation rate is found to be proportional to a Boltzmann factor with the activation energy given by an effective trap depth, i.e. the minimal kinetic energy ions need to escape from the trap. We study this effective trap depth as a function of the applied rf amplitude and find two distinct regimes. Based on numerical calculations, the steeply rising trap depth for low rf amplitudes is explained by an entirely adiabatic motion of the trapped ions, whereas the regime of almost constant trap depth for high rf amplitude shows the appearance of regions of unstable ion motion inside the trap. An analytical model allows us to predict the parameters for a maximum trapping potential and trapping volume.

The 22pole ion trap used in our experiment [19] approximates a multipole rf field of order  $n = 11$ . Storage is achieved by 22 stainless steel rods (1 mm diameter) forming a 40 mm long cylindrical cage (inscribed diameter  $2r_0 = 10$  mm, see schematic view in Fig. 1). The rods are alternately connected to the two ports of an rf oscillator ( $\omega = 2\pi \times 4.7$  MHz) providing a cylindrical effective potential in the radial direction. Along the axis ions are confined by small dc voltages (3-10 V) applied to cylindrical entrance and exit electrodes. We manipulate the temperature of the ion ensemble via heating or cooling the trap and its housing, into which we apply helium at

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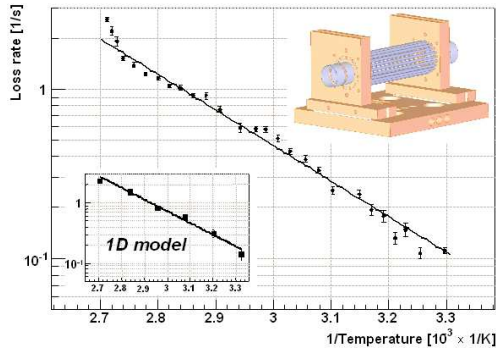


FIG. 1: Measured loss rate of  $\text{Cl}^-$  anions out of the 22pole trap (see schematic view) versus temperature at an rf amplitude of  $V_0 = 33$  V. The solid line is a fit to Eq. (1). A similar result is obtained with a 1D numerical model (see inset) in the same temperature range at an rf amplitude of  $V_0 = 10.5$  V.

a well defined density of typically  $2 \times 10^{14} \text{ cm}^{-3}$ . Thermalization of the ions hence occurs on the timescale of  $100 \mu\text{s}$ , assuming a Langevin-limited collision rate. The ion source employs a pulsed supersonic expansion of argon with a small admixture of  $\text{CCl}_4$  bombarded by a pulsed 1 keV electron beam. In the created local plasma  $\text{Cl}^-$  ions are formed via dissociative attachment of slow electrons to  $\text{CCl}_4$  and transferred to the trap with a time-of-flight Wiley-McLaren mass spectrometer. To optimize the trapping efficiency ions are initially trapped at a fixed rf amplitude for 200 ms, which is then ramped down linearly within 100 ms to the desired value. Typically  $2 \times 10^3$   $\text{Cl}^-$  anions are trapped per filling, which results in a Spitzer self collision time [6] of about 40 s at 300 K, ensuring that ion-ion interactions do not play a role. After extraction the ions are mass analyzed in a second time-of-flight stage before being detected on a microchannel plate.

We observe that the loss rate of  $\text{Cl}^-$  anions from the trap depends strongly on their temperature as can be seen from Fig. 1. For this measurement we heat the trap to 370 K and measure the loss rate while slowly cooling the trap to 300 K. Each loss rate is derived by measuring the decay of the chlorine anion peak in the mass spectrum when increasing the storage time. It is important to note that we do not observe any other peaks in the mass spectra for any of the storage times. Actually, chemical reactions with any of the possible impurities in the background gas are not expected considering the high electron affinity of chlorine of 3.6 eV. Destruction of the anions through detachment of the excess electron by blackbody radiation is excluded on this timescale regarding the high photon energies needed. Similarly, detachment by collisions can be excluded in the temperature regime under study. This indicates, that the ions are physically removed from the trap and that the only possible loss process from the trap is evaporation over the effective energy

barrier formed by the rf field. This is strongly supported by the dependence of the loss rate on the temperature of the ion ensemble. Fig. 1 reflects that by increasing its temperature we force more ions over the barrier.

We fit the measured loss rate  $k(T)$  to a Boltzmann factor

$$k(T) = A \times e^{-\frac{E_a}{k_B T}}, \quad (1)$$

with the activation energy for loss of anions  $E_a$  and the pre-exponential factor  $A$  as free parameters.  $E_a$  is directly obtained in units of the Boltzmann constant  $k_B$  as the slope of the fit in Fig. 1.  $E_a$  represents the kinetic energy ions need to exceed the effective barrier formed by the rf field and therefore provides an elegant way to determine the effective trap depth. We have determined the effective trap depth of the 22pole ion trap as a function of the applied rf amplitude  $V_0$ . Experimental accuracies are derived from the Boltzmann fits. As can be seen from Fig. 2 the effective trap depth  $U(V_0)$  rises steeply for low rf amplitudes  $V_0$  and reaches a maximum of 0.65 eV at around 12 V. For higher amplitudes  $U(V_0)$  decreases slightly before it eventually levels off at 0.5 eV for amplitudes  $V_0 > 40$  V. This shows that trapping is characterized by two distinct regimes, one with a fast increasing trap depth and one where the depth is roughly constant. In addition a small dip in the measured effective trap depth is observed at an rf amplitude of 30 V.

Additional evidence for the two different evaporation regimes stems from the pre-exponential factor  $A$  in equation (1). For large rf amplitudes  $A$  is found to be of the order of  $10^7/s$ , which fits best to the frequency of the field, and is independent of the helium density up to  $2 \times 10^{15} \text{ cm}^{-3}$ . For very small rf amplitudes  $A$  is two to three orders of magnitude smaller and compares well with the collision frequency of the anions with the helium buffer gas.

To get a microscopic insight into the involved loss processes, we have set up a simple numerical model; details will be published elsewhere.  $\text{Cl}^-$  ions are propagated in a one-dimensional oscillating electric multipole field of order  $n$  [27]  $E(r, t) = \frac{V_0}{r_0} n |r|^{n-1} \cos(\omega t + \Phi)$  with  $-r_0 \leq r \leq +r_0$  by solving the equation of motion numerically. We record the loss of ions starting at  $r = 0$  with random phase  $\Phi$  with an initial velocity drawn from a Maxwellian distribution. The inset in Fig. 1 shows the temperature dependence of the loss rate. In analogy to the experiment we determine the height of the effective barrier as a function of the rf amplitude. As seen in Fig. 2b the numerically determined effective barrier height rises steeply for low rf amplitudes, reaches a maximum and then slightly decreases for high amplitudes. This behavior is consistent with the corresponding experimental data in Fig. 2a. In detail, however, there are distinct differences in the maximum barrier height and its corresponding rf amplitude. Nevertheless, the simple 1D model provides valuable insight. The initial velocities of those ions lost during propagation demonstrate that exclusively hot ions in the Boltzmann tail of the distri-

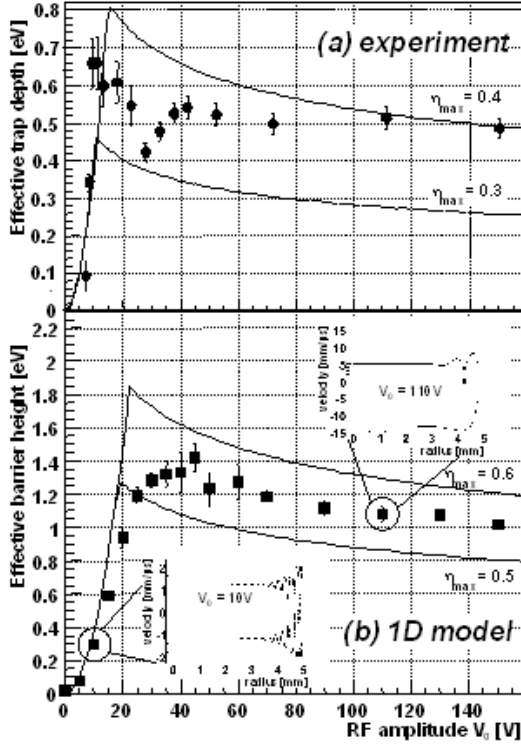


FIG. 2: Experimentally determined effective trap depth (a) and numerically obtained effective barrier height (b) as a function of the rf amplitude. Each point is derived from a fit similar to Fig. 1. Inserted lines stem from the analytical model for different parameters of the maximum adiabaticity parameter  $\eta_{max}$ . The two inserted phase space trajectories represent ions with a starting velocity just below the threshold for direct escape. At low rf amplitudes the ion returns from the barrier with the initial velocity. Strong transfer of energy from the field to the ion motion is seen at high rf amplitudes.

bution are lost, which backs our analysis of evaporation-driven ion loss. The calculated ion trajectories in phase space are characterized by a uniform velocity in the region of low field at smaller radii evolving into a fast oscillation of the velocity in the region of high field near the turning point. For a small rf amplitude  $V_0$  where in Fig.2b the effective barrier height is found to be steeply rising, no transfer of energy from the field is observed. Either the ions are reflected from the flapping potential, preserving their kinetic energy, or their initial kinetic energy exceeds the effective barrier and ions are lost on first approach. The inset in Fig.2b for an rf amplitude of  $V_0 = 10$  V shows such a trajectory for an ion starting with a velocity just below the limit for getting lost. For high rf amplitudes, however, ions with an initial velocity just below the limit for getting lost on the first approach are found to rapidly acquire energy from the field. This can be seen from the trajectory shown in Fig.2b for an rf amplitude of  $V_0 = 110$  V, where the ion velocity on return is more than twice the initial value. The ion will not survive the next approach to the barrier.

By comparison with the numerical simulation we are able to interpret the abrupt break-off in the experimentally observed effective trap depth shown in Fig.2a and the accompanied change in the pre-factor  $A$  to a value of the order of the rf frequency. We identify it with the advent of non-adiabatic ion motion. Ions are lost from the trap by rapidly acquiring translational energy from the rf field within a few rf cycles, once they happen to be located in a trap region where the rf amplitude is strong enough to disturb adiabatic motion.

For an analytic description of the trap depth we introduce the trapping volume as the volume in which stable trajectories without transfer of energy from the field are possible. The numerical simulation shows in agreement with our measurement that the trapping volume is reduced for increasing rf amplitude and that the reduction prevails over the increase in the repelling force by the rf field. We parameterize the trapping volume based on the adiabaticity parameter  $\eta$  defined in [27], which scales with the  $(n-2)$ -power of the radial position of the ion. We consider the trapping volume to be bound by a critical radius  $r_{crit}$  where  $\eta = \eta_{max}$  if this radius is smaller than the geometrical radius  $r_0$  of the trap, otherwise by  $r_0$ . We then identify the time-independent effective potential at the edge of the trapping volume with the effective trap depth. This results in an effective trap depth of an ideal multipole trap of

$$U(V_0) = \frac{1}{8} \frac{(qV_0)^2}{\epsilon} r_{tv}^{2n-2} \quad (2)$$

where  $r_{tv} = \text{Min}\{r_0, r_{crit}\}$  is the radius of the trapping volume,  $r_{crit}$  the critical radius

$$r_{crit} = r_0 \left( \eta_{max} \frac{n}{n-1} \frac{\epsilon}{qV_0} \right)^{1/(n-2)}, \quad (3)$$

and  $\epsilon = 1/(2n^2)m\omega^2 r_0^2$  the characteristic energy. For low rf amplitudes  $V_0$  the adiabaticity parameter  $\eta$  does not exceed  $\eta_{max}$  in the entire trap. Here the trapping volume equals the geometrical volume of the trap and the effective trap depth is given by the effective potential at radius  $r_0$ . In this regime, the effective trap depth grows quadratically with the applied rf amplitude  $V_0$ . The maximal trap depth is obtained, when  $\eta$  reaches the largest allowed value  $\eta_{max}$  just at the geometrical edge of the trap. For higher amplitudes, the region of non-adiabatic ion motion begins to penetrate into the trap. The trapping volume is now bound by the condition  $\eta = \eta_{max}$  and the effective trap depth is given by the effective potential at this reduced radius, which scales as  $V_0^{-2/9}$ .

The lines in Fig.2a represent the effective trap depth  $U(V_0)$  according to the described analytical model for  $\eta_{max}$  between 0.3 and 0.4. With these values the experimental data are very well described. Also the numerical result in Fig.2b is described well by Eq. (2), however with a higher value of the maximal adiabaticity parameter  $\eta_{max}$  of between 0.5 and 0.6. This difference might

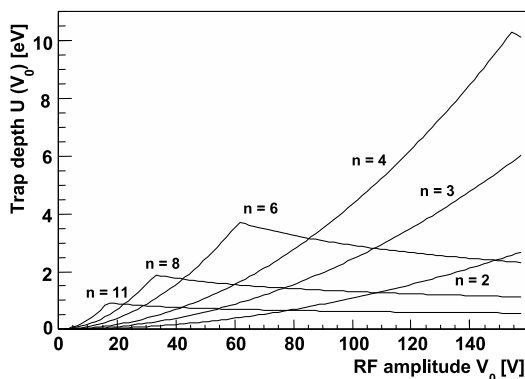


FIG. 3: Effective trap depths for multipoles of different order  $n$  as derived from the analytical model assuming a maximum adiabaticity parameter  $\eta_{max} = 0.4$  (calculation for  $\text{Cl}^-$  ions,  $r_0 = 5$  mm,  $\omega = 2\pi \times 5$  MHz).

be explained by weak fringe fields disturbing the perfect multipole configuration which could originate from charge up of insulators and residual gas deposited onto the electrodes. This is supported by the experience that multipole ion traps provide longer lifetimes immediately after cooling down as compared to many days of operation at low temperatures. The dip in the effective trap depth observed at amplitudes around 25 V is currently unexplained and subject to further work.

The analytical and numerical models can be readily applied to multipoles of different order  $n$ . In Fig. 3 the effective trap depth for  $\text{Cl}^-$  ions is plotted as a function of the rf amplitude for various multipoles of the same inscribed radius  $r_0 = 5$  mm operated at a fixed frequency  $\omega = 2\pi \times 5$  MHz assuming a maximum adiabaticity parameter  $\eta_{max} = 0.4$ . The larger field-free region for increasing multipole order  $n$  is paid by a smaller maximal effective trap depth. Also, lower order multipole traps can be operated in an all-adiabatic mode up to higher rf amplitudes. For a quadrupole trap ( $n = 2$ ) the adia-

baticity parameter  $\eta$  becomes independent of the radius, but is still a function of the rf amplitude  $V_0$ . Note that this results in a distinct difference to higher order multipoles: The trap depth scales quadratically with the rf amplitude  $V_0$  until the maximal stability parameter is reached; at this point there is a transition from adiabatic to nonadiabatic ion motion in the entire trap and the trap depth vanishes completely.

In conclusion, we demonstrate evaporation of anions out of a multipole rf ion trap. Analysis of the temperature-dependent evaporation rate allows us to extract the effective trap depth. This shows that Boltzmann statistics are not only applicable to the translational and rotational degrees of freedom of the bulk of trapped ions [16], but also to the high-energy tail of the Boltzmann distribution. Furthermore, we observe the transition from an all-adiabatic trapping to energy transfer from the field to the ion motion. Based on a numerical calculation we introduce the concept of a trapping volume, and by its parameterization we obtain an analytic expression for the effective trap depth and its scaling with the rf amplitude, which is directly applicable to multipole fields of arbitrary order  $n$ .

The present results suggest possible applications of trap losses as a probing scheme for inelastic collision processes of trapped ions, similar to schemes used for neutral atoms [28, 29]. Maximizing the trapping volume of multipole traps based on our findings should allow one to trap an optimum number of ions at a given space charge interaction, which is particularly interesting for the loading of shallow surface traps [30]. Furthermore, ion-ion induced evaporation in a collision free environment may be investigated, for which we have first experimental evidence at larger ion ensembles.

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